Improving the dispersion of silica fume in cement pastes and mortars

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Abstract. There are many possibilities how to improve concrete properties such as compressive strength, flexural strength, durability, and others. The change in the composition of ordinary Portland concrete (OPC) is one possible way. This change may result in the formation of concrete with added properties known as high-performance concrete (HPC). Traditional methods used to receive high-performance concrete design and manufacture emphasize the removal of coarse aggregates. This is achieved by using the specially sorted fine aggregates at relatively low doses along with super-plasticizers and silica fume. Problem with fine reactive aggregates is their agglomeration which causes reduction of the reactive surface. This work is focused on evaluation of the ultrasound technology for the dispersion of silica fume. For comparison, different cement mixtures were prepared to study the effects of the treatment of silica fume prior to its use in HPC applications.

1. Introduction

Silica fume (microsilica) is well known supplementary cementitious material which is used in cement mixtures to affect microstructure with focus to interfacial zone between binder – aggregate. Silica fume is the byproduct of producing silicon metal or ferrosilicon alloy. Silicon vapor released from the furnace oxidizes and forms small spherical particles, which are collected in silos. Besides silica fume which is an industrial by-product, natural Pozzolans are known. These natural Pozzolans are mostly of volcanic origin.

A most common form of silica fume used in current concrete practice is in dry powder form, the alternative is slurried silica fume. Dry powder usually consists of agglomerates which can be a size up to several millimeters and they are generally not dispersable into individual silica fume spheres under conventional concrete mixing. Substantial content of agglomerates almost always remain in the concrete. The size of undispersed agglomerates remaining in the cement matrix after mixing can be bigger than the particles of used cement. This is very limiting for the potential benefits regarding fine particle filler effect [1].

Silica fume is a high surface material. The surface is usually measured by absorption of nitrogen and results show that the surface area of silica fume is around 20 000 m²/kg. For example values of the surface area of Portland cement measured by the absorption of nitrogen is around 1 500 m²/kg. Together with the high values of the surface area, the amorphous character of SiO₂ in the silica fume which gives high potential to react in the Pozzolanic reactions is very advantageous property. Surface area is very important and can be increased by precise deagglomeration of the raw microsilica powder [2].
The reaction between the particles of amorphous SiO$_2$, portlandite (Ca(OH)$_2$) and water create products similar to hydration of Portland cement, well known as the calcium–silicate–hydrate (C–S–H) gel. Crystals of portlandite are consumed by this reaction. Residual portlandite can have a negative influence on the mechanical properties due to its low compressive strength. Pozzolan reaction is shown in equation (1). Its rate is slower then hydration of cement minerals and secondary C–S–H* gel makes structure much more compact [3].

At early stages (within a few hours of hydration), the extra surface of the pozzolan results in acceleration of the overall hydration kinetics by enhanced heterogeneous nucleation of C–S–H gel [4]. This acceleration effect is typically termed as the filler effect, in the filler term material is described as chemically inert material [5],[6]. Formation of secondary pozzolanic C–S–H* gel, results in improvement of solid to solid state connectivity in the microstructure of the matrices, lead to improvement in materials properties, such as higher compressive strength and improved durability [7].

$$\text{puzzolan} + \text{CH} + \text{H} \rightarrow \text{C-S-H}^*$$

(1)

* secondary C-S-H gel

Elimination of agglomerates can be accomplished by many ways such as grinding or mixing. Both of these methods have physical limitations of deagglomeration and can add impurities because the sample is in direct contact with the mill. On the other hand, ultrasonication of liquid suspensions of powders can provide different possibilities for agglomeration reduction. Because there is no direct contact between the sample particles and ultrasonic source, contamination of the product is minimal after the ultrasonication. Mechanism of deagglomeration by using sonication is described by the interaction of agglomerates with collapsing cavities or with other particles [8].

During the ultrasonication, agglomerates interact with cavities which are caused by the propagation of mechanical waves in the liquid. The sound waves that propagate into the liquid media result in alternating high-pressure (compression) and low-pressure (rarefaction) cycles. The individual particles can be held together by different attraction forces on physical or chemical nature. Ultrasonic cavitation in liquids causes high-speed liquid jets. This jets press liquid at high pressure between the particles and separate them from each other [9].

There is very strong interest in the reasonable use of secondary materials. According to this fact, it is necessary to utilize the highest potential properties of each component in the concrete. Deagglomeration and increasing silica fume surface area among possible ways how to improve the mechanical properties of the concrete. For this reason ultrasonication technology was chosen, which can be easily introduced into industry and result in better function of the silica fume in concrete production.

2. Materials and methods
Silica fume ELKEM Micsrosilica 920E and Portland cement CEM I 42,5 R plant Mokrá were used for the mixtures. For improving rheological properties superplasticizer MasterGlenium ACE 446 which allowed the low water-binder ratio was used. Two different aggregates for mortars, normalized sand PG II and calcinated bauxite were used. To achieve a similar particle size distribution of aggregates bauxite was sieved on 0.75 mm and 1.25 mm mesh sieves. The fraction between the sieves was analyzed by laser analysis of particle size (HELOS KR Sympatec) and compared with the PG II (middle sand according to ČSN EN 196–1)). Figure 1 and Figure 2 show the particle size distribution of the aggregates. Figure 3 and Figure 4 show the particle size distribution of Portland cement and undispersed silica fume.
Table 1. Particle size distribution.

| Sample         | D_{50} (µm) | D_{90} (µm) | Modus (µm) |
|----------------|-------------|-------------|-------------|
| CEM I 42.5 R   | 8.91        | 35.18       | 22.51       |
| Silica fume    | 5.92        | 14.95       | 11.7        |
| PG II          | 806.58      | 1047.06     | 796.93      |
| Bauxite        | 837.05      | 1084.26     | 796.93      |

Table 1 shows the characteristical values of the measured materials. Modus value of the aggregates is the same and D_{50} and D_{90} are very similar. The particle size of the binder materials (silica fume and cement) are different. Silica fume before using ultrasonication contains two times smaller particles and it can provide the effect of the filler in the samples.

The composition of prepared samples is shown in Table 2. All samples had a similar W/B (water/binder) ratio 0.3 and dose of the plasticizer was counted as 1.2% of the binder components (cement + puzzolan). Cement pastes with number 1 contain no aggregates other samples contain 50% aggregates counted to all other components. All mixtures were prepared in three different ultrasonication times 0, 5 and 35 minutes. Mixing of the components was performed according to valid standard ČSN EN 196-1.

For the mixtures, without ultrasonication, the superplasticizer was dissolved in water and added to the cement and silica fume in the mixer. Producing samples of mortars the aggregates were added
to this mixture after 30 seconds of mixing. For samples where the sonication was used, the silica fume was mixed with the water and superplasticizer. This suspension was then ultrasonified for 5 and 35 minutes. After the ultrasonication, it was added to the mixer with cement and in the case of mortars, the aggregates were added later on, after 30 seconds od mixing.

For structure observation the scanning electron microscope Zeiss EVO LS 10 was used. Samples were covered with golden/platinum layer for better conduction of electron. Conditions of the measurement accelerating voltage 15 kV and current to 100 pA were set.

Table 2. The composition of the prepared samples.

| Sample | 1 | 1U | 1UU | 2_Kp | 2_KpU | 2_KpUU | 3_Kb | 3_KbU | 3_KbU |
|--------|---|----|-----|------|-------|--------|------|-------|-------|
| CEM I 42.5 R [g] | 3672 | 3672 | 3672 | 1836 | 1836 | 1836 | 1836 | 1836 | 1836 |
| Silica fume [g] | 324 | 324 | 324 | 324 | 324 | 324 | 324 | 324 | 324 |
| PG II [g] | 0 | 0 | 0 | 2160 | 2160 | 2160 | 0 | 0 | 0 |
| Bauxite [g] | 0 | 0 | 0 | 0 | 2160 | 2160 | 2160 | 0 | 0 |
| H2O [g] | 1296 | 1296 | 1296 | 648 | 648 | 648 | 648 | 648 | 648 |
| W/B | 0.3 | 0.3 | 0.3 | 0.3 | 0.3 | 0.3 | 0.3 | 0.3 | 0.3 |
| Superplasticizer [g] | 51.8 | 51.8 | 51.8 | 25.9 | 25.9 | 25.9 | 25.9 | 25.9 | 25.9 |
| Sonification [min] | 0 | 5 | 35 | 0 | 5 | 35 | 0 | 5 | 35 |

3. Results and discussion

For dispergation by sonification ultrasonic bath Bandelin DT 514 H was used. Table 3 shows the properties of the ultrasonic bath.

Table 3. Properties of Bandelin DT 514 H ultrasonic bath.

| Internal dimensions [mm] | Container volume [l] | Ultrasonic power $P_{eff}$ [W] |
|--------------------------|----------------------|-------------------------------|
| 325 x 300 x 150          | 13.5                 | 215                           |

Consumption of the energy by the ultrasonic bath for the dispergation of silica fume was calculated according to equation (2) and (3). Time of dispergation was 0, 5 or 35 minutes and the values energy consumed are 64.5 kJ for 5 minutes of sonification and 451.5 kJ for 35 minutes. When $W$ is work, $P$ stands for ultrasonic power and $t$ for time of ultrasonication.

$$W = P \cdot t = 215 \cdot 300 = 64500 \text{ J} = 64.5 \text{ kJ}$$

$$W = P \cdot t = 215 \cdot 2100 = 451500 \text{ J} = 451.5 \text{ kJ}$$

Mechanical properties were tested on three 40 x 40 x 160 mm test specimens for each sample and day of storage. Data were measured by equipment for testing of building materials (DESTTEST, BETONSYSTEM). The average values of compressive strength are shown in Figure 5.
Figure 5. The compressive strength of prepared samples.

Generally, the compressive strength can be seen as the trend of gradual increase of strength in time. Each sample was prepared in three different ways with the same chemical composition. These three different ways of mixture preparation showed different values of the strength. In sample 1 and 2, the lowest compressive strength shows the mixtures with a short time of sonification. Highest compressive strength shows mixtures with 35 minutes of sonification and the lowest compressive strength shows mixtures with no sonification.

The mixture number three with calcinated bauxite as an aggregate showed different results. It was assumed that using aggregate with higher compressive strength will result in higher compressive strength of the mortar but the trend will be preserved. Sample 3 which contains calcinated bauxite showed different mechanical properties.

Sample batch 1 (paste) and 2 (mortar with PG II) exhibit the same trend in compressive strength increase. Lowest compressive strength was observed in the samples with 5 minutes of sonification. Samples with no sonification shown middle values of compressive strength and highest compressive strength were observed with 35 min of sonification. This trend is caused by different stages of sonification. In the first stage, the silica fume particles are hitting each other and making bigger agglomerates [10]. During this time it was necessary to mix the silica fume suspension and exhibit the sedimentation of silica fume agglomerates. After approximately 15 minutes of sonification, there is no need for the mixing of the suspension because silica fume particles are small enough, that buoyancy force is bigger than the gravity force. This is the reason why the 5 minutes of sonification has a negative influence on the compressive strength of the samples 1 and 2.

In sample batch 3, which contain bauxite as the aggregate it was observed, that with increasing time of dispersation, also the compressive strength was increased. This is probably caused by the different shape of the bauxite. Bauxite is agglomerate with higher mechanical properties than the quartz. Grinding of the bauxite is performed by dynamical forces during the crushing which results in the different shape of the bauxite particles [11].

This particle shape has a very big influence on the dispersation of the silica fume agglomerates because it acts as a sharp blade which can cut the agglomerates compared to the quartz spherical
particles. Literature shows that there is a clear relationship between shape, texture, and grinding of aggregates and the voids content of aggregates. This fact supports the theory about the shape influence on the mixing and deagglomeration of the silica fume. The deagglomeration of the mixing, in case of bauxite, exceeded the deagglomeration by the ultrasonic disperser [12].

Figure 6. SEM picture of sample 3_Kb.

Figure 7. SEM picture of sample 3_KbUU.

Figure 6 and Figure 7 shows SEM pictures of the same mixtures with different time of sonification. Both pictures were taken at the magnification 20 000x. There is no significant proof of silica fume dispersion on figure 6. On the Figure 7 more homogenous distribution of silica fume particles can be observed.

4. Conclusion

This work focuses on the improvement of silica fume dispersion in cement pastes and mortars by using basic laboratory equipment such as ultrasonic disperser. Idea for using the ultrasonication was the low price of the equipment and its presence in every laboratory.

The main focus of this work was to show the effect of the sonification on the mechanical properties according to mixture composition. An assumption was that all mixtures will increase their mechanical properties (compressive strength) with increasing time of ultrasonication. From the measured data can be observed, that mixtures containing calcinated bauxite as an aggregate showed a different behavior than mixtures containing normalized sand and pastes.

The pastes and mortars with sand showed the lowest compressive strength after 5 minutes of ultrasonication. This results can be explained by the fact that during the first phase of ultrasonication agglomerates are binding with each other and form bigger agglomerates. In the second phase, the cavitation is overcoming the cohesive force of agglomerates and results in deagglomeration of silica fume particles.

In the mixtures with calcinated bauxite the different shape of calcined bauxite particles plays an important role. Normalized sand particles are spherical compared to plane particles of bauxite. These plane particles act as small blades which have a big impact on silica fume agglomeration during the mixing.

Continuous research will focus on the different phenomena of hydration curves between dispersed and undispersed silica fume particles and their puzzolan activity.

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