The Effect of Silica Fume Addition on the Resistance of Concrete to Alkali Silica Reaction

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Abstract. Concrete mix made of cement CEM I 42.5 R, silica fume, fine aggregate sand of 0/4 fraction and superplasticizer was tested. Five batches of specimens were made with different silica fume content, where up to 10 % of the binding material was replaced with silica fume. Compressive strength, water absorption, density and resistance to alkali silica reaction were tested in concretes modified with different amounts of silica fume addition. The effect of silica fume addition on the expansion of modified concrete conditioned in 1M NaOH solution for 56 days was tested. Concrete modified with silica fume at 10 % by weight of cement was found to be the most appropriate for structures exposed to alkaline environment. The control specimen without mineral addition had the expansion of 0.113 %, which exceeds the limit value by 0.1 %, whereas the expansion of specimens modified with 2.5 % of silica fume was equal to the limit value, i.e. 0.1 %. The expansion values reduced in specimens modified with 5 % and 7.5 % of mineral addition. After 56 days of testing, the expansion values of these specimens were 0.093 % and 0.082 % respectively. The lowest expansion value was obtained in specimens with the highest content of silica fume, i.e. 10 %. The expansion of these specimens was 0.07 % after 56 days of conditioning in 1M NaOH solution of 80 ºC temperature. The tests revealed that concrete modified with silica fume replacing 10 % of cement had better resistance to alkali silica reaction and better durability characteristics and thus can be used as structural concrete.

1. Introduction

Concrete is the most widely used construction material worldwide, with billions of tons produced every year [1]. During the last three decades, great strides have been made in improving the performance of concrete as a construction material [2]. Durability of ordinary Portland cement is of a major issue in civil infrastructure projects [3].

Modern concrete is more than just a mixture of cement, water, and aggregates. Modern concrete more and more often contains mineral components having very specific characteristics that give specific properties to concrete, and also chemical admixtures that have even more specific effects [4].

Concrete consists of aggregate particles, water, and a binding agent (cement and other cementitious materials). The reactions between aggregates and binding agents are extremely complex. Many natural aggregates contain amorphous silica and carbonate, which both react with the alkalis (Na and K) that are released into the mixture from cementitious materials. This interaction is widely known as the alkali-aggregate reaction (AAR). Depending on which minerals are involved, AAR is subdivided into alkali-silica reaction (ASR) and alkali-carbonate reaction (ACR). ASR is generated by the aggregates containing reactive silica minerals [5].
After more than 60 years of research, the knowledge gained on reaction mechanisms has allowed researchers and recommendation committees to provide rules to prevent new ASR cases [6]. Unfortunately, no ways to stop the reaction or to cure an affected structure have been found until now. There are many ASR affected structures around the world which require periodical repairs and preventive maintenance policies creating to ongoing costs [7].

The product of alkali-silica reaction is a gel that surrounds the aggregate in the concrete matrix. This gel can appear as a dark border around the aggregate or a white spot within the aggregate, sometimes the white area extending into the concrete matrix [8]. ASR is a chemical process occurring within the concrete, in which alkali, mostly originating from cement, react with silica originating from the aggregate [9]. Water plays a major role in the degradation of structures affected by ASR [10].

The reaction of amorphous or crystalline SiO$_2$ fume aggregates with the alkaline pore solution of concrete (pH 13.0–13.5) causes the expansion of concrete. The generated stress may eventually cause cracks in concrete years after the affected structures were built [11]. ASR affected concrete structures exhibit cracking, displacements, structural deformations, pop-outs and reduction in mechanical performance. Service of structures may be severely affected. Gels are usually supposed to be the main cause of the induced swelling and degradation [12].

The formation of the ASR gel alone does not cause cracking; however, when the gel absorbs water, it has a significant potential to swell. The resulting expansion often results in pressures greater than concrete can withstand, which in turn causes cracks in the concrete. The ASR is a multistage process [13-14].

For the design of a concrete mix, it is important to consider the fine particles, as they have an influence on the water demand and, consequently, on the fresh and hardened concrete properties [15].

Different mineral admixtures are often added in concrete to improve the durability, rheology of fresh concrete, and mechanical properties of hardened concrete [16]. Silica fume, a by-product of the ferrosilicon industry, is a highly pozzolanic material that is used as mineral admixture to enhance mechanical and durability properties of concrete. Silica fume (SF) is added to concrete to improve strength and reduce permeability [17]. SF concrete may be appropriate in places where high abrasion resistance and low permeability are of utmost importance or where very high cohesive mixes are required to avoid segregation and bleeding [2]. It may be added directly to concrete as an individual ingredient or in a blend of Portland cement and silica fume [18]. Silica fume can be used in a densified or undensified powder form, a slurry, as a combination at the concrete mixer, or part of a factory-blended cement [19]. Individual particles are extremely small, approximately 1/100th the size of an average cement particle. Because of its fine particles, large surface area, and high SiO$_2$ content, silica fume is a very reactive pozzolan when used in concrete [20]. Silica induces a pozzolanic reaction that results in the reduction of the amount of calcium hydroxide in concrete, and SF reduces porosity and improves durability [21].

Alkali-aggregate reaction has always been and will always be a concern for the construction industry because there is currently no way to completely cure the problem before it stops by itself, which can take decades to happen after extensive damage has developed [22].

This paper reports the results of research into the effect of liquid suspension of amorphous silica fume on the resistance of concrete containing reactive aggregates to alkali silica reaction. The aim of the paper is to analyse the effect of silica fume addition on alkali silica reaction in concrete mixture containing reactive aggregates.

2. Materials and test methods

Portland cement CEM I 42.5 R and liquid suspension of amorphous SF (as mineral addition) were used for the tests. Chemical compositions of cement and liquid suspension of amorphous silica fume are presented in Table 1 and Table 2. Sand of fraction 0/4 mm was used for the test. Sand specifications are presented in Table 3.

The concrete mix was prepared in accordance with the requirements of standard EN 196-1:2016. 5 batches of concrete mixes were mechanically produced under laboratory conditions for the tests. The
batches differed by the type of cement and silica fume content ranging from 0% to 10% by weight of cement (the binder was replaced by silica fume). Compositions of concrete mixtures are presented in Table 4. Concrete mixes were mechanically mixed under laboratory conditions and 40×40×160 mm size specimens were formed in metal casting moulds. Specimens were removed from the moulds after 24 hours of curing and soaked in 20±2°C water for 28 days. After 7 and 28 days of curing in water of 20 ± 2 °C temperature the density of the specimens was measured according to EN 12390-7:2009, the compressive strength was measured according to EN 12390-3:2009/AC:2011. The total water absorption of the specimens was measured after soaking in water for 96 hours. The specimens were soaked in water of 20 ± 2°C temperature and kept there until the constant mass was achieved. Specimens in the bath must be placed at 15 mm between specimens and the layer of water above the specimens must be at least 20 mm. The constant mass was achieved when the difference in weight every 24 hours was less than 0.1 %. Prior to weighting the specimens were dried with a damp cloth to remove excessive water.

Table 1. Chemical composition of cement.

| Chemical composition, % | SiO₂ | Al₂O₃ | Fe₂O₃ | CaO | K₂O | SO₃ | Na₂O | Na₃O | Other |
|-------------------------|------|-------|-------|-----|-----|-----|------|------|-------|
|                        | 20.76| 6.12  | 3.37  | 63.5| 1   | 0.8 | 0.3  | 0.8  | 3.35  |

Table 2. Chemical composition of liquid suspension of amorphous SF.

| Chemical composition | SiO₂ | Al₂O₃ | Fe₂O₃ | CaO | MgO | K₂O | Na₂O | Na₃O | SO₃ | Loss on ignition |
|----------------------|------|-------|-------|-----|-----|-----|------|------|-----|-----------------|
|                      | 93.35| 0.92  | 0.71  | 0.69| 0.72| 0.86| 0.33 | 0.85 | 0.13| 1.44            |

Table 3. Mineral and petrographic composition of sand from used quarries.

| Mineral and petrographic composition | Sand fraction 0/4 |
|--------------------------------------|-------------------|
| Quartz                              | 62.3 %            |
| Feldspars                           | 13.0 %            |
| Carbonates                          | 14.2 %            |
| Mica                                | 0.1 %             |
| Amphiboles                          | 2.6 %             |
| Crystal rock                        | 7.8 %             |

Table 4. Compositions of concrete mixes.

| SF content, % (by weight of cement) | Cement, % | Aggregate, % | Water, % | Silica fume, % | W/C | Plasticizer, % (by weight of cement) | Slump flow, mm |
|------------------------------------|-----------|---------------|----------|----------------|-----|--------------------------------------|----------------|
| 0                                  | 26.88     | 60.48         | 12.63    | 0.00           | 0.47| 0                                    | 205            |
| 2.5                                | 26.21     | 60.48         | 12.63    | 0.67           | 0.47| 0.20                                 | 219            |
| 5                                  | 25.54     | 60.48         | 12.63    | 1.34           | 0.47| 0.30                                 | 215            |
| 7.5                                | 24.87     | 60.48         | 12.63    | 2.02           | 0.47| 0.60                                 | 205            |
| 10                                 | 24.19     | 60.48         | 12.63    | 2.69           | 0.47| 0.80                                 | 205            |

The resistance of concrete specimens to ASR was tested in accordance with the standardised methodology Rilem AAR–2. According to AAR-2 method the specimens (40x40x160 mm) are cured in water of 80 °C and further conditioned in 1M NaOH solution of 80 °C for 14 days; afterwards their expansion is measured. The methodology prescribes a longer conditioning time for specimens with
aggregates containing slowly reactive rocks. In our case the time of soaking specimens in 1M NaOH solution was extended to 56 days [23].

For ASR tests washed samples are dried at 100 °C–110 °C for 16 hours. The mortar was made of 1 part cement and 2.25 parts of aggregate. 600 g of cement and 1350 g of dry aggregate is required for three prisms (40×40×160 mm). The water/cement ratio was 0.47. The mortar flow diameter must be from 205 to 220 mm. Polycarboxylate-based superplasticizer was used to obtain the required mortar flow.

Four prisms with each silica fume amount were selected for the test. The prisms were immersed into water of 80 °C. After 24 hours the distance between the inner ends of the metal pins were measured and the specimens were placed into stainless steel containers with 1M NaOH alkali solution at 80 °C. Containers with the specimens were placed into climatic chamber where 80 ± 2 °C temperature was maintained. The elongation of specimens was measured regularly. The specimens were removed after 24 ± 2 hours of hardening in water at 80 °C temperature, and the length, i.e. the zero reading (L0) was recorded; this is a reference reading for further measuring of specimen expansion. After the specimens were placed into 1M NaOH alkaline solution at 80 °C, the specimen dimensions (Ln) were recorded after 1, 3, 6, 9, 12, 14, 21, 28, 35, 42, 49, 56 days ± 2 hours. The elongation of specimens was measured by a digital dial indicator with the scale interval of 0.001 mm. The indicator was fixed in the frame where the prisms were placed. The frame and indicator axles were inserted into the moulded holes at the ends of the specimen.

The linear expansion of each specimen was obtained by calculating the difference between the length of the specimen at each period of measurement (Ln) and zero measurement (L0), to the nearest 0.001% of the effective length, as follows:

\[
\text{Expansion, } \% = \frac{100 \cdot (L_n - L_0)}{l}
\]

Where:

L0 - measurement of the specimen just before the immersion into sodium hydroxide solution (zero reading),

Ln - a reading taken at each period of soaking in sodium hydroxide solution, n being the number of days counted from the zero reading.

l - distance between the inner ends of the metal pins, measured to the nearest of 0.1 mm.

According to RILEM AAR-2 method, aggregates are considered to be reactive when the expansion of concrete specimens conditioned in 1M NaOH solution for 14 days exceeds 0.054 % [24]. According to ASTM C 441 test method, in tests lasting for 56 days the threshold expansion limit is 0.1 %.

3. Test results and analysis

Figure 1 illustrates density and water absorption tests of concrete modified with silica fume.

![Figure 1. Relationship between density and water absorption of concrete and silica fume content.](image-url)
The results of tests of concrete modified with silica fume revealed that the highest density of 2131 kg/m$^3$ was obtained in the batch containing 10% of silica fume. It was found that the density of specimens was directly related to silica fume content, i.e. the higher amount of silica fume was added to the mix, the higher density of the specimen was obtained. The maximum difference in the density between control specimens and the specimens containing 10% of silica fume is 100 kg/m$^3$, i.e. 4.92%.

Water absorption rate decreases after silica fume is added to concrete mix. A minimum drop of 0.01% of water absorption value (3.99%) was recorded in specimens where 2.5% of the binder was replaced with silica fume. When silica fume content was increased to 5% and 7.5%, water absorption values reduced to 3.95% and 3.91%. In specimens with the maximum SF content of 10% the lowest water absorption value was 3.8%, which is 0.2% lower than water absorption in control specimens.

Figure 2 illustrates the relationship between the compressive strength of concrete cured for 7 and 28 days and silica fume content.

The mean value of control specimen’s compressive strength after 7 days of curing is 46.78 MPa. An increase of 4.05 MPa was observed in specimens where 2.5% of the binder was replaced with SiO$_2$. These specimens had the compressive strength of 50.83 MPa. Specimens modified with 5% of silica fume had the compressive strength of 54.05 MPa, i.e. 7.27 MPa higher compared to the control specimen. When silica fume content was increased up to 7.5%, the compressive strength reached 56.98 MPa. After 7 days of curing specimens with the maximum 10% content of silica fume had the compressive strength of 57.39 MPa, which was 22.68% higher compared to the control specimen containing no silica fume.

The compressive strength values increase with higher SF content after 28 days of curing. When cement is replaced with 2.5% of silica fume, the compressive strength increases by 3.51%, i.e. from 52.08 MPa (control specimen) to 53.91 MPa. When 5% and 7.5% of the binding material is replaced with silica fume, the compressive strength values increase 9.12% and 10.06% and reach 56.83 MPa and 57.32 MPa. The highest compressive strength value (59.06 MPa) was obtained with the highest silica fume content (10%). The compressive strength of those specimens was 13.4% higher compared to the control specimen.

![Figure 2. Relationship between the compressive strength of concrete after 7 and 28 days of curing and silica fume content.](image_url)

Silica fume fills in small voids in concrete structure and increases concrete density, ultrasonic pulse velocity, compressive and flexural strength, but reduces water absorption. Concrete structure becomes more homogeneous, the porosity reduces and the connection between the aggregate and cement matrix becomes stronger.

The highest density, ultrasonic pulse velocity, compressive and flexural strength values, and the lowest water absorption value were obtained when concrete was modified with 10% of silica fume.
Figure 3 illustrates the relationship between the expansion of silica fume modified concrete specimens made of cement CEM I 42.5 R and silica fume content in the mix after conditioning the specimens in 1M NaOH solution at 80 ºC temperature for 56 days. Constant increase of expansion was observed.

![Graph showing expansion vs. days for different silica fume contents](image)

**Figure 3.** Relationship between the expansion of silica fume modified concrete specimens and silica fume content after conditioning in 1M NaOH solution of 80 ºC for 56 days.

The test results showed that in specimens containing 0 %, 2.5 %, and 5.0 % of silica fume addition the average expansion values after 14 days exceeded the allowable expansion limit of 0.054 %. In specimens where 7.5 % and 10.0 % of cement was replaced with silica fume addition the respective expansion values were 0.039 % and 0.042% after 14 days of testing.

After conditioning in the specimens 1M NaOH solution of 80 ºC for 56 days, the control specimen without mineral additions had the expansion of 0.113 %, which exceeds the limit value by 0.1 %, whereas the expansion of specimens modified with 2.5 % of silica fume was equal to the limit value, i.e. 0.1 %. The expansion values reduced in specimens modified with 5 % and 7.5 % of mineral addition. After 56 days of testing the expansion values of these specimens were 0.093 % and 0.082 % respectively. The lowest expansion value was obtained in specimens with the highest content of silica fume, i.e. 10 %. The expansion of these specimens was 0.07 % after 56 days of conditioning at 80 ºC temperature in 1M NaOH solution.

The test method used revealed that the limit value of silica fume in concrete made of cement CEM I 42,5 R without mineral addition and reactive aggregates is 7.5 %. After 14 and 56 days of testing the expansion of specimens made of concrete mix modified with 7.5 % silica fume did not exceed the threshold expansion limit values of 0.054 % and 0.1 %.

Figure 4 illustrates the relationship between the expansion of specimens conditioned in 1M NaOH solution of 80 ºC for 14 and 56 days and silica fume content.

Tests with different amounts of silica fume revealed that the absolute lower expansion values are obtained in specimens where 10 % of the binding material (CEM I 42.5 R) was replaced. SiO₂ was found to have a positive effect on concrete with reactive aggregates in ASR favourable environment.

ASR induced expansion of modified concrete specimens after 14 and 56 days of conditioning in 1M NaOH solution of 80 ºC depends on the amount of tested mineral additions and SiO₂ content in them.
Figure 4. Relationship between the expansions of concrete specimens conditioned in 1M NaOH solution of 80ºC temperature for 14 and 56 days and silica fume content in the mix.

A higher content of active mineral addition in concrete mix causes a bigger amount of alkali present in the cement to react and thus reduces the amount of reactive aggregate and alkali reaction product and expansion of concrete.

4. Conclusions
It was found that 10% of silica fume addition by weight of cement increases the density, compressive strengths, and reduces water absorption of concrete. Higher density and lower water absorption hinder corrosion in alkaline environment, i.e. water absorption by the gel and the development of destructive internal stresses are impeded.

Direct influence of silica fume on the corrosion in alkaline environment was determined by the tests. The expansion of specimens decreases with higher silica fume content. The test results showed that the expansion values in specimens made of concrete mix of cement CEM I 42.5 R without silica fume and in specimens made of concrete mix with the same type of cement modified with 10.0% of silica fume by weight of cement, reduces from 0.076% to 0.039% after 14 days and from 0.113% to 0.070% after 56 days of testing.

The limit value of silica fume in concrete mix was established. The expansion of specimens does not exceed the threshold limit value of 0.054% after 14 days of testing and 0.1% after 56 days of testing when concrete mix is modified with 7.5% of silica fume by weight of cement.

Amorphous SiO₂ rich silica fume used in concrete manufacture causes a bigger amount of alkali present in the cement to react and thus reduces the amount of reactive aggregate and alkali reaction product and expansion of concrete.

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